

In-Plane Aromaticity in Cycloparaphenylene Dications: A Magnetic Circular Dichroism and Theoretical Study

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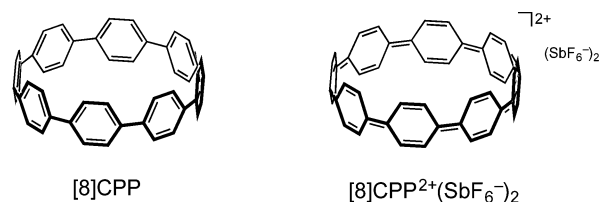
S Supporting Information

ABSTRACT: The electronic structures of [8]cycloparaphenylene dication ([8]CPP²⁺) and radical cation ([8]CPP^{•+}) have been investigated by magnetic circular dichroism (MCD) spectroscopy, which enabled unambiguous discrimination between previously conflicting assignments of the UV–vis–NIR absorption spectral bands. Molecular orbital and nucleus-independent chemical shift (NICS) analysis revealed that [8]CPP²⁺ shows in-plane aromaticity with a (4*n* + 2) π -electron system (*n* = 7). This aromaticity appears to be the origin of the unusual stability of the dication. Theoretical calculations further suggested that not only [8]CPP²⁺ but also all [*n*]CPP (*n* = 5–10) dications and dianions exhibit in-plane aromaticity.

Cycloparaphenylenes (CPPs) are hoop-shaped conjugated hydrocarbons consisting of benzene rings linked at the para positions.¹ Their π -orbitals lie parallel to the macrocyclic ring plane, and their molecular structures can be regarded as carbon nanotube fragments. Because of their unique topology, these macrocycles have attracted considerable attention, not only because of their theoretical interest but also because of their possible applications in materials science. Since the first successful synthesis in 2008,² several research groups have developed syntheses of [*n*]CPPs of different ring sizes (where *n* represents the number of benzene units).³ The effect of the size of [*n*]CPPs on the electronic properties has been intensively investigated by various techniques.⁴

Recently, one of our groups synthesized the radical cation and dication of [8]CPP ([8]CPP^{•+} and [8]CPP²⁺, respectively) by chemical oxidation of [8]CPP with NOSbF₆ or SbCl₅ (Chart 1).⁵ These oxidized forms were both surprisingly stable, despite a lack of steric protection. They exhibit an intense absorption band in the near-infrared (NIR) region, and their spin and cationic charge are fully delocalized over the ring. Jasti et al. also reported the isolation of [8]CPP^{•+} by chemical oxidation of [8]CPP and described the formation of a charge-resonance dimer (([8]CPP₂)^{•+}) by reaction of the radical cation with neutral [8]CPP.⁶ However, there is a significant discrepancy between the two reports regarding the band assignments of the oxidized species in the UV–vis–NIR

Chart 1. Structures of [8]Cycloparaphenylene and Its Dication



spectra; the dication and the radical cation in our study showed the same spectra as the radical cation and the dimer, respectively, reported by Jasti. Herein, we report a definitive assignment of the absorption spectra of the dication and the radical cation by means of magnetic circular dichroism (MCD) spectroscopy, which can provide valuable information about the electronic structures of cyclic π -conjugated molecules.⁷ We also discuss the origin of the peculiar stability and electronic structure of [*n*]CPP dications on the basis of density functional calculations and theoretical chemistry. Although molecular orbitals of CPPs have already been reported,^{4d,5,6,8} our present findings establish the existence of in-plane aromaticity of [8]CPP²⁺ with a (4*n* + 2) π -electron system (*n* = 7) for the first time, on the basis of molecular orbital analysis and nucleus-independent chemical shift (NICS) calculations.⁹ This finding provides an explanation for the unusual stability of the dication. Further calculations indicated that not only [8]CPP but also all [*n*]CPP (*n* = 5–10) dications and dianions possess (4*n* + 2) π -electrons and thus show in-plane aromaticity. Schleyer et al. theoretically predicted in-plane aromaticity in trannulenes, in which the C–C double bonds in the ring are exclusively in trans configuration,¹⁰ and this prediction was verified in highly substituted C₆₀ derivatives with a (4*n* + 2) π -electron system (*n* = 4).¹¹ However, our results demonstrate the existence of a new type of in-plane aromaticity with an all-*cis*-annulene pathway.

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The dication of [8]CPP was prepared as reported in our previous paper.⁵ Figure 1 shows the electronic absorption and

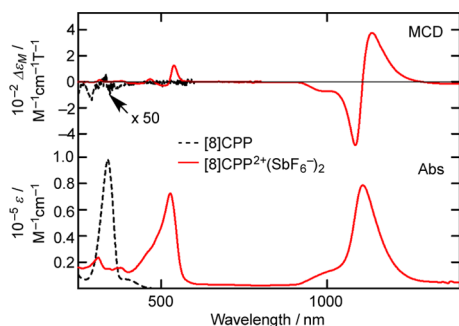


Figure 1. MCD (top) and electronic absorption (bottom) spectra of [8]CPP²⁺(SbF₆⁻)₂ (red solid line) and [8]CPP (black broken line) in CH₂Cl₂ at room temperature under an argon atmosphere.

MCD spectra of [8]CPP²⁺(SbF₆⁻)₂ and [8]CPP in dichloromethane at room temperature. The most prominent feature of the MCD spectrum of the dication is the distinctive derivative-shaped signal in the NIR region. This type of MCD signal can be assigned as the Faraday A term, due to transition from the nondegenerate ground state to the degenerate excited state.⁷ The sign of the A term is negative, implying that the orbital angular momentum is greater in the ground state than in the excited state.¹² This result is consistent with our previous assignment, based on time-dependent density functional theory (TDDFT) calculations, that this absorption band arises from the transition from the doubly degenerate HOMOs to the nondegenerate LUMO (Figure 2a).⁵ The MCD intensity for the visible absorption band was considerably weaker than that for the near-IR band, but a clear MCD signal with a negative Faraday A term was observed. This result is also consistent with the TDDFT-based attribution of the band to transition from the HOMOs to nondegenerate LUMO + 1.⁵ The appearance of two negative Faraday A terms in the NIR and visible regions was reproduced by TDDFT calculations (see Supporting Information),¹³ strongly supporting the validity of this characterization of the dication.

Next, the MCD spectrum of the radical cation ([8]-CPP^{•+}SbF₆⁻) was measured (see Supporting Information). An intense negative Faraday A term was observed for the broad absorption band in the near-IR region, though solvent peaks were superimposed. This is also in agreement with the TDDFT-based conclusion that the near-IR band is due to the transition from the doubly degenerate HOMOs to SOMO.⁵ Jasti et al. observed the same spectra and attributed the broad absorption to the charge-resonance transition of a charge-resonance dimer (([8]CPP₂)^{•+}).⁶ Since the charge-resonance transition is expected to be nondegenerate and would not show the Faraday A term, their band assignment is inconsistent with the present results. In contrast to the intense MCD signals of the dication and radical cation, the MCD intensities of the neutral form were much weaker (Figure 1).

To gain further insights into the anomalous stability of the dication, we carried out a molecular orbital analysis. Figure 2a shows the frontier molecular orbitals of [8]CPP²⁺. The numbers of nodes in the HOMOs, LUMO, and LUMO + 1 of the dication are 7, 8, and 8, respectively. The nodal patterns and the degeneracy of the HOMO are exactly the same as those of all-*cis*-[32]annulene¹⁴ dication, although the energy

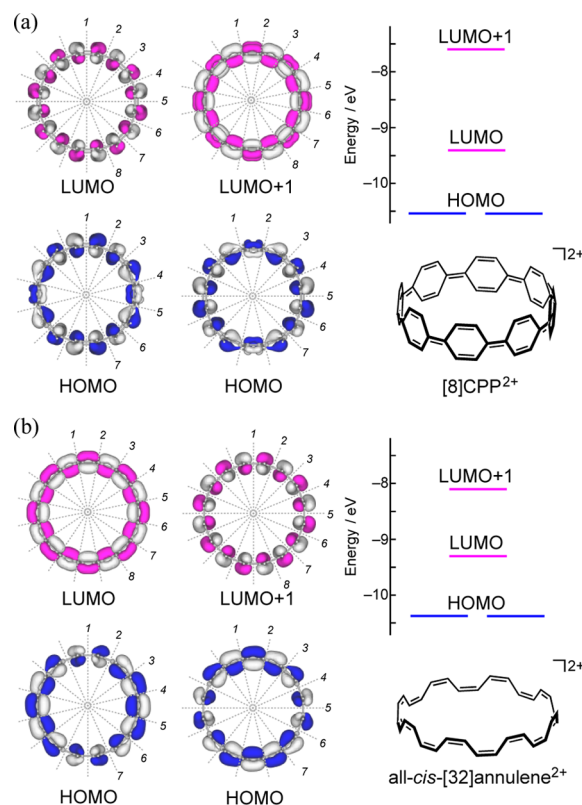


Figure 2. Frontier molecular orbitals and energy levels of the optimized structures of [8]CPP²⁺ (a) and all-*cis*-[32]annulene dication (b). Calculations were performed at the B3LYP/6-31+G(d) level. Arbitrary nodal lines are drawn on the iso-surface plots.

ordering of the LUMO and LUMO + 1 is different (Figure 2b). The nodal patterns are also identical to those of [32]trannulene dication (Supporting Information), which has a $(4n + 2)$ π -electron system ($n = 7$),¹⁰ while the LUMO is doubly degenerate, unlike those of [8]CPP²⁺ and all-*cis*-[32]annulene dication, due to the difference in molecular symmetry. In addition, the number of nodes in the four orbitals of [8]CPP²⁺ is the same as that of the 30 π -electron aromatic cyclo[8]pyrrole dication reported by Waluk et al.^{12,c,d} These results strongly suggest that the electronic structure of [8]CPP²⁺ can be expressed as a $(4n + 2)$ π -electron system ($n = 7$) and that [8]CPP²⁺ possesses in-plane aromaticity.¹⁵

The aromatic character of [8]CPP²⁺ was further studied by means of NICS calculations. As shown in Figure 3a, the NICS value at the center of the ring in [8]CPP²⁺ (-13.99 ppm) was strongly negative. This value is somewhat less than that of [32]trannulene dication (-18.35 ppm) but is comparable to the NICS value of all-*cis*-[32]annulene dication (-11.70 ppm). The small difference in the values for [8]CPP²⁺ and all-*cis*-[32]annulene dication may be due to eight additional C-C double bonds, which generate macrocyclic π -circuits other than the all-*cis*-[32]annulene pathway. Strongly negative NICS values of [8]CPP²⁺ were also calculated at different levels of theory (HF/6-311+G(d,p)), -17.34 ppm; B3LYP/6-311+G(d,p), -14.35 ppm). These results indicate the existence of diatropic ring currents caused by cyclic delocalization of π -orbitals of [8]CPP²⁺, which is consistent with the experimental observation that the proton NMR signal of [8]CPP²⁺(SbF₆⁻)₂ is shifted upfield to 5.24 ppm.⁵

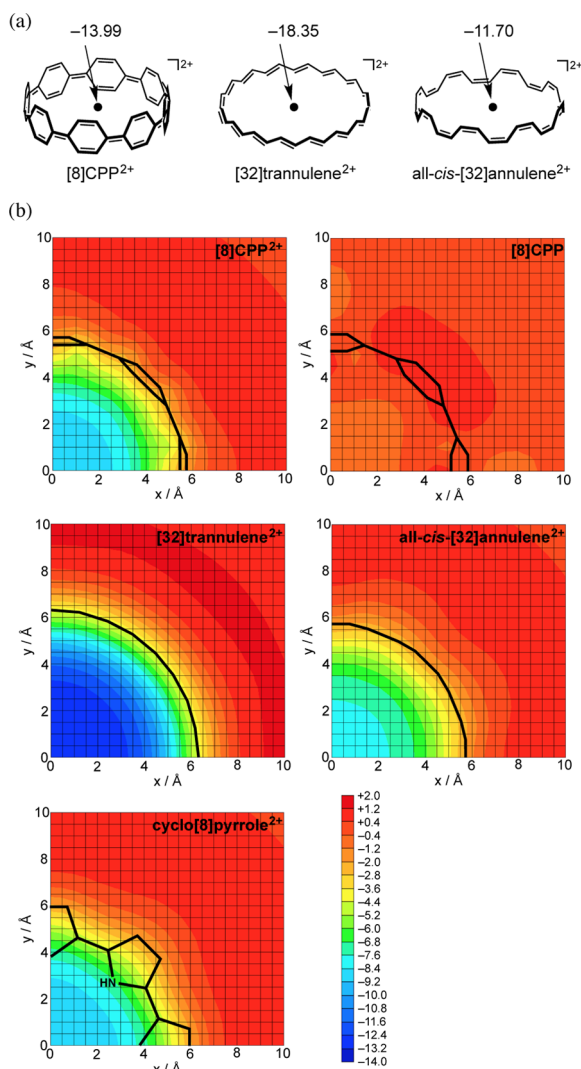


Figure 3. (a) NICS (ppm, B3LYP/6-31+G(d)) calculated for the optimized structure of [8]CPP²⁺, [32]trannulene dication, and all-*cis*-[32]annulene dication. (b) Contour plots of NICS (ppm, B3LYP/6-31+G(d)) at 3.0 Å above the median plane of [8]CPP²⁺, [8]CPP, [32]trannulene dication, all-*cis*-[32]annulene dication, and cyclo[8]-pyrrole dication.

To visualize the ring current effect, contour plots of NICS at 3.0 Å above the median plane of a series of macrocycles were computed.¹⁶ As shown in Figure 3b, negative NICS values were calculated over the inside of the nano hoop of [8]CPP²⁺. The appearance of the contour plot was similar to those of [32]trannulene dication and all-*cis*-[32]annulene dication, but was completely different from that of [8]CPP. Since the NICS value at the center of the ring in 30 π -electron aromatic cyclo[8]pyrrole dication (-14.20 ppm) and its NICS contour plots are similar to those of [8]CPP²⁺, the ring current effect of in-plane aromaticity should be as large as that of

conventional aromaticity. These results strongly suggest that this aromatic stabilization is the origin of the anomalous stability of [8]CPP²⁺.

The existence of in-plane aromaticity should extend to all CPP dications ([*n*]CPP²⁺) because they all have $(4(n - 1) + 2)$ π -electrons, while neutral [*n*]CPP has $4n$ π -electrons. Similarly, CPP dianions ([*n*]CPP²⁻) with $(4n + 2)$ π -electrons should also have in-plane aromaticity. To clarify this point, NICS calculations were conducted for the dication, neutral form, and dianion of [*n*]CPPs ($n = 5-10$), and the results are summarized in Table 1. All the dications and dianions have strongly negative NICS values, as expected, whereas the values of neutral [*n*]CPPs are small in magnitude. The numbers of nodes in the HOMO and LUMO of [*n*]CPP dications were $n - 1$ and n , whereas those of the dianions were n and $n + 1$. All these results clearly indicate that these [*n*]CPPs dications and dianions are aromatic compounds. The neutral forms can be regarded as nonaromatic because of the small negative NICS values. The negative values may arise from the diatropic ring currents of the benzene units (see Supporting Information).

The absolute values of NICS for the dication and dianion forms increase with decreasing size of the CPP rings (Table 1). This trend is associated with the structural properties of the CPP rings (see Supporting Information). Thus, an increase in the quinoidal contribution with small dihedral angles of the adjacent two *para*-phenylene units seems to be related to the increase in the absolute values of NICS.

In summary, the electronic absorption bands of the [8]CPP dication and radical cation have been definitively assigned on the basis of MCD spectroscopy and theoretical calculations. Analyses of the nodal patterns of the frontier molecular orbitals and NICS calculation of [8]CPP²⁺ revealed that the electronic structure of the dication can be regarded as a $(4n + 2)$ π -electron system ($n = 7$) with in-plane aromaticity. Extension of the analysis revealed that not only [8]CPP dication but also all [*n*]CPP ($n = 5-10$) dications and dianions are in-plane aromatic compounds having $(4n + 2)$ π -electrons, i.e., the neutral form of [*n*]CPP is a $4n$ π -electron in-plane nonaromatic system. The facile generation and extra stability of [8]CPP²⁺(SbF₆⁻)₂ are thus considered to be due to this aromatic stabilization. These results also suggest that dianions of CPPs should be isolable as stable forms. Our findings represent an important step toward fully understanding the unique electronic structure of CPPs, and we believe that dication and dianion of CPPs will prove to be useful tools for obtaining novel aromatic molecules. Preparation and isolation of [*n*]CPP²⁻ are currently being examined in our laboratory.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures, spectral data, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Table 1. NICS (ppm, B3LYP/6-31+G(d)) Calculated for the Optimized Structures of the Dication, Neutral Form, and Dianion of [*n*]CPPs

<i>n</i>	5	6	7	8	9	10
[<i>n</i>]CPP ²⁺	-19.63	-18.28	-16.41	-13.99	-12.30	-10.52
[<i>n</i>]CPP	-1.26	-2.90	-2.52	-2.26	-1.88	-1.60
[<i>n</i>]CPP ²⁻	-16.65	-16.61	-15.47	-13.75	-12.31	-10.81

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Notes

The authors declare no competing financial interest.

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- (15) As the NIR and visible absorption bands of [8]CPP²⁺ are derived from the same transitions as those of cyclo[8]pyrrole dication, these bands can be labeled as L and B transitions. The sign of the Faraday A term for conventional cyclic molecules with a $(4n + 2)$ π -electron system depends on the difference in the orbital angular momentum between the excited electron and hole. According to Michl's perimeter model, negative Faraday A terms are observed for the L and B transitions of aromatic molecules having degenerate HOMOs and nondegenerate LUMO.¹⁷ The present system has degenerate HOMOs and nondegenerate LUMO, so the perimeter model seems to be applicable to in-plane aromatic molecules.
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